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TITLE: Alkali-soluble copolymer capable of giving much higher viscosity when dissolved, used in a thickener for e.g. paints for buildings, comprises polymerization product of an alkenylether, acidic monomer and its salt

PATENT-ASSIGNEE: NIPPON SHOKUBAI CO LTD[JAPC]

PRIORITY-DATA: 2000JP-0052609 (February 28, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
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APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2001240630A	N/A	2000JP-0052609	February 28, 2000

INT-CL (IPC): C08F002/22, C08F290/04 , C08G065/329 , C09K003/00

ABSTRACTED-PUB-NO: JP2001240630A

BASIC-ABSTRACT:

NOVELTY - New alkali-soluble copolymer is made by polymerization of an alkenylether, acidic monomer and its salt. The copolymer is capable of giving much higher viscosity when dissolved, and is used in a thickener in paints for buildings, synthetic water preserver, concrete separation inhibitor, etc.

DETAILED DESCRIPTION - A copolymer comprises an alkenylether of formula (I) and an acidic monomer (and/or its salt).

n = average number 10-300;

R = hydrocarbon group; and

X = -C(O)- or -C(O)NH-

USE - The new copolymer is used in an alkali-soluble thickener.

ADVANTAGE - Product is soluble in alkaline solution and strikingly enhances viscosity when dissolved.

CHOSEN-DRAWING: Dwg.0/8

TITLE-TERMS: ALKALI SOLUBLE COPOLYMER CAPABLE HIGH VISCOSITY
DISSOLVE THICKEN
PAINT BUILD COMPRISE PRODUCT ACIDIC MONOMER SALT

DERWENT-CLASS: A25 A82 A93 G02 L02

CPI-CODES: A04-F11; A09-A; A12-W12; G02-A03; L02-D14M; L02-D14R;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; H0022 H0011 ; G0022*R D01 D51 D53 D11 D10 D58 D95 F34 H0215
; G0022*R D01 D51 D53 D60 D61*R ; L9999 L2528 L2506 ; L9999 L2551
L2506 ; H0282

Polymer Index [1.2]

018 ; H0022 H0011 ; G0022*R D01 D51 D53 D11 D10 D58 D95 F34 H0215
; R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D60
D84 F36 F35 ; L9999 L2528 L2506 ; L9999 L2551 L2506 ; H0282 ; P0088

Polymer Index [1.3]

018 ; H0033 H0011 ; G0022*R D01 D51 D53 D11 D10 D58 D95 F34 H0215
; G0022*R D01 D51 D53 D60 D61*R ; R01126 G0340 G0339 G0260 G0022
D01 D11 D10 D12 D26 D51 D53 D58 D63 D85 F41 F89 ; L9999 L2528 L2506
; L9999 L2551 L2506 ; H0282 ; P0088

Polymer Index [1.4]

018 ; H0033 H0011 ; G0022*R D01 D51 D53 D11 D10 D58 D95 F34 H0215
; R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D60
D84 F36 F35 ; R01126 G0340 G0339 G0260 G0022 D01 D11 D10 D12 D26
D51 D53 D58 D63 D85 F41 F89 ; L9999 L2528 L2506 ; L9999 L2551 L2506
; H0282 ; P0088

Polymer Index [1.5]

018 ; ND01 ; ND09 ; ND03 ; B9999 B5652 B3521 B3510 B3372 ; B9999
B3678 B3554 ; Q9999 Q7158*R Q7114 ; Q9999 Q6951*R Q6939 ; Q9999

* NOTICES *

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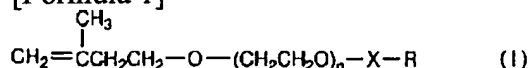
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CLAIMS

[Claim(s)]

[Claim 1] The copolymer to which it comes to carry out the polymerization of the monomer component containing the alkenyl ether monomer which consists of a reactant polymer shown by the following general formula (1), and an acid monomer and/or its salt.

[Formula 1]



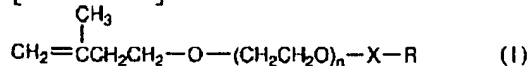
(However, 10-300R of n are hydrocarbon groups by the average, and X is -C(O)- or -C(O) NH-.)

[Claim 2] The copolymer according to claim 1 said whose polymerization is an emulsion polymerization.

[Claim 3] The copolymer according to claim 1 or 2 with which said copolymer is used as an alkali fusibility thickener.

[Claim 4] The reactant polymer shown by the following general formula (1).

[Formula 2]



(However, 10-300R of n are hydrocarbon groups by the average, and X is -C(O)- or -C(O) NH-.)

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is meltable in an alkali solution, and when it dissolves, it relates to the new copolymer which can raise the viscosity. Moreover, by carrying out a polymerization, this invention is meltable in an alkali solution, and when it dissolves, it relates to the new reactant polymer which can turn into a polymer which can raise the viscosity.

[0002]

[Description of the Prior Art] The copolymer meltable in the alkali solution obtained by copolymerizing the monomer which has an acidic group is known variously. Although there is a copolymer which the hydrophobic groups in a copolymer meet and raises thickening nature (JP,58-189299,A, JP,8-225618,A, the patent No. 2553841 official report), for example, it is used as a thickener also among these copolymers after dissolving in an alkali solution, development of the copolymer which has still higher thickening nature is expected.

[0003]

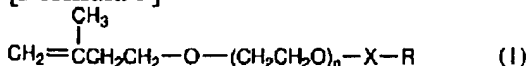
[Problem(s) to be Solved by the Invention] Then, the technical problem which this invention tends to solve is meltable in an alkali solution, and when it dissolves, it is to offer the new copolymer which can raise the viscosity by leaps and bounds.

[0004]

[Means for Solving the Problem] By inquiring wholeheartedly, in order to solve the above-mentioned technical problem, and raising the hydrophobicity of a hydrophobic group, this invention person thought that viscosity would raise by leaps and bounds, acquired the check by experiment, and reached this invention. That is, the copolymer concerning this invention comes to carry out the polymerization of the monomer component containing the alkenyl ether monomer which consists of a reactant polymer shown by the following general formula (1), and an acid monomer and/or its salt.

[0005]

[Formula 3]



[0006] (However, 10-300R of n are hydrocarbon groups by the average, and X is -C(O)- or -C(O)NH-.) Moreover, the reactant polymer concerning this invention is shown by the above-mentioned general formula (1).

[0007]

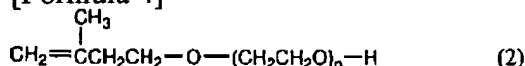
[Embodiment of the Invention] The reactant polymer concerning this invention is shown by the general formula (1), and is a monomer which a radical (3-methyl-3-butenyl) and R (hydrocarbon group) come to join together through a divalent oxyethylene radical. Since the hydrophobic radicals which consist of R (hydrocarbon group) meet strongly, when the polymer obtained by carrying out the polymerization of this monomer dissolves in an alkali solution, it can raise that viscosity by leaps and bounds. R in a

general formula (1) is a hydrocarbon group, and its hydrocarbon group of carbon numbers 6-30 is desirable, for example, polycyclic type alkyl groups, such as alkyl aryl radical; cyclo octyl radicals, such as aryl group; nonylphenyl radicals, such as alkyl group; phenyl groups, such as an octyl radical, a nonyl radical, dodecyl, and an octadecyl radical, a naphthyl group, and an anthryl radical, and a dodecyl phenyl group, a cholesteryl radical, and a llano SUTANIRU radical, can be mentioned, and these one sort or two sorts or more are used. Also in these, the hydrocarbon group of carbon numbers 8-30 is desirable, the alkyl group of carbon numbers 8-30 is more desirable, the alkyl group of carbon numbers 12-20 is more desirable, the alkyl group of carbon numbers 16-20 is still more desirable, and the alkyl group of a carbon number 18 is the most desirable.

[0008] By the average, n in a general formula (1) is 10-300, is 20-80 preferably [it is desirable and] to 10-100, and a pan, is 40-60 especially preferably, and is 45-55 most preferably. About the manufacture approach of the alkenyl ether monomer shown by the general formula (1), especially limitation can mention the approach of of the following (a) and (b) which uses as a raw material the compound a (polyoxyethylene [3-methyl-3-butenyl] ether (the end of a polyoxyethylene radical is a hydroxyl group)) which there is not, for example, is shown by the following general formula (2). In addition, the compound a of a raw material can be manufactured to an isoprene by carrying out specified quantity addition of the ethylene oxide for water after 1 molecule addition.

[0009]

[Formula 4]



[0010] (However, n is 10-300 by the average.)

(a) How to be a reaction with (Approach b) compounds a and RCOOM (for M to be an alkyl group or hydrogen) which obtain the alkenyl ether monomer of $\text{X}=\text{C}(\text{O})\text{NH}-$, and to obtain the alkenyl ether monomer of $\text{X}=\text{C}(\text{O})-$ at a reaction with Compounds a and RNCO.

The reactant polymer of this invention is used for carrying out a polymerization like the after-mentioned and manufacturing the copolymer of this invention etc., and also it can be used for applications, such as a modifier of various polymers. The copolymer concerning this invention carries out the polymerization of the monomer component containing the alkenyl ether monomer (it may only be hereafter called "the alkenyl ether monomer shown by the general formula (1)") which consists of a reactant polymer shown by the general formula (1), and an acid monomer and/or its salt, and is obtained.

[0011] As for the blending ratio of coal of the alkenyl ether monomer shown by the general formula (1), it is desirable that it is 0.01 - four-mol % to all monomers, and it is 0.04 - one-mol % more preferably. When said blending ratio of coal is less than [0.01 mol %], and the amounts of the hydrophobic radical of the copolymer of this invention run short and it dissolves in an alkali solution, the effectiveness which raises the viscosity becomes low. If the amount exceeding four-mol % is used, when it will become difficult to manufacture a copolymer by the emulsion polymerization on the other hand, a meeting of the hydrophobic radicals within the same polymer increases, and the effectiveness which raises viscosity falls. The copolymer of this invention can serve as alkali fusibility by copolymerizing an acid monomer and/or its salt. As this acid monomer and/or its salt For example, an acrylic acid, a methacrylic acid, an acryloxy propionic acid, Carboxyl group content monomers, such as a citraconic acid, an itaconic acid, a crotonic acid, a maleic acid, and a maleic anhydride; A vinyl sulfonic acid, Sulfonic group content monomers, such as a styrene sulfonic acid and sulfoethyl (meta) acrylate; Monochrome (2-methacryloyloxy-ethyl) phosphate, Monochrome (2-acryloyloxyethyl) phosphate, 2-(meta) acryloyloxypropyl phosphate, Phosphoric-acid radical content monomers [, such as 2-(meth) acryloyloxy-3-chloropropyl phosphate and 2-(meta) acryloyloxyethyl phenyl phosphate,]; and these salts can be mentioned, and these one sort or two sorts or more are used. Also among these, a carboxyl group content monomer and/or its salt are desirable. A carboxyl group content monomer and/or its salt have a comparatively low hydrophilic property compared with other acid radical content monomer and/or its salt, and this is because the stability at the time of a polymerization is high. Also in a carboxyl

group content monomer and/or its salt, since copolymeric [with other monomers] is good as for at least one sort chosen from an acrylic acid, methacrylic acids, and these salts, it is desirable.

[0012] As a salt of an acid monomer, metal salts, such as sodium salt of the acid above-mentioned monomer and potassium salt, ammonium salt, etc. can be mentioned, and these one sort or two sorts or more are used. 10-70-mol% of the blending ratio of coal of an acid monomer and/or its salt is desirable to all monomers, and is 20-60-mol % more preferably. Since it is hard to carry out alkali soluble when said blending ratio of coal is less than [10 mol %], sufficient thickening nature is not obtained. On the other hand, when exceeding 70-mol %, polymerization stability in an emulsion polymerization cannot be maintained.

[0013] Moreover, at least one sort of blending ratio of coal [10-70 mol% of] chosen from an acrylic acid, methacrylic acids, and these salts is desirable to all monomers, and is 20-60-mol % more preferably. Since it is hard to carry out alkali soluble when said blending ratio of coal is less than [10 mol %], sufficient thickening nature is not obtained. On the other hand, when exceeding 70-mol %, polymerization stability in an emulsion polymerization cannot be maintained. The monomer component used as the raw material of the copolymer of this invention may contain the alkenyl ether monomer shown by the general formula (1), and these monomers other than an acid monomer and/or its salt and the ethylenic unsaturated monomer which can be copolymerized.

[0014] As an ethylenic unsaturated monomer, for example Styrene, vinyltoluene, Styrene system polymerization nature monomers, such as alpha methyl styrene, ethyl vinylbenzene, and chloro methyl styrene; (meta) Acrylamide, N-monomethyl (meta) acrylamide, N-monoethyl (meta) acrylamide, Acrylamide (meta) system polymerization nature monomers, such as N and N-dimethyl (meta) acrylamide; (meta) A methyl acrylate, An ethyl acrylate, (Meta) (Meta) acrylic ester system polymerization nature monomer; (meta) which is ester of acrylic acids (meta), such as butyl acrylate, and the alcohol of carbon numbers 1-8 (meta) -- cyclohexyl radical content polymerization nature monomers [, such as acrylic-acid cyclohexyl,]; (meta) -- acrylic-acid 2-hydroxyethyl -- 2-hydroxypropyl acrylate etc. (Meta) (Meta) hydroxyl content (meta) acrylic ester system polymerization nature monomer; which is monoester of an acrylic acid and a polyalkylene glycol -- polyethylene-glycol chain content polymerization nature monomers [, such as polyethylene-glycol (meta) acrylic ester,]; -- vinyl acetate; -- Acrylonitrile; N-vinyl pyrrolidone, acrylic-acid (meta) dimethylaminoethyl, (Meta) Dimethylaminoethyl (meta) acrylamide, dimethylaminopropyl (meta) acrylamide, Basic polymerization nature monomer; N-methylol (meta) acrylamides, such as vinylpyridine and a vinyl imidazole, Cross-linking (meta) acrylamide system polymerization nature monomers, such as N-butoxy methyl (meta) acrylamide; Vinyltrimethoxysilane, Vinyltriethoxysilane, gamma-(meta) acryloyl propyltrimethoxysilane, The hydrolysis nature silicon radical content polymerization nature monomer linking directly to silicon atoms, such as a vinyl tris (2-methoxyethoxy) silane and allyl compound triethoxysilane; (meta) Metaglycidyl acrylate, Epoxy group content polymerization nature monomers, such as acrylic glycidyl ether; 2-isopropenyl-2-oxazoline, Oxazoline radical content polymerization nature monomers, such as 2-vinyl oxazoline; (meta) Acrylic-acid-2-aziridinyl ethyl, Aziridine radical content polymerization nature monomers, such as a bitter taste roil aziridine; (Meta) Halogen content polymerization nature monomers, such as vinyl fluoride, vinylidene fluoride, a vinyl chloride, and a vinylidene chloride, etc. can be mentioned, and these one sort or two sorts or more are used.

[0015] 30-90-mol% of the blending ratio of coal of an ethylenic unsaturated monomer is desirable to all monomers, and is 40-80-mol % more preferably. When said blending ratio of coal is less than [30 mol %], polymerization stability in an emulsion polymerization cannot be maintained. On the other hand, since it is hard to carry out alkali soluble when exceeding 90-mol %, sufficient thickening nature is not obtained. A monomer component may contain a cross-linking monomer further. As a cross-linking monomer, for example An acrylic acid (meta) and ethylene glycol, 1, 3-butylene glycol, a diethylene glycol, 1,6-hexanediol, Neopentyl glycol, a polyethylene glycol, propylene glycol, A polypropylene glycol, trimethylol propane, pentaerythritol, To intramoleculars, such as methylene (meta) acrylamide, The polyfunctional (meta) acrylic ester system polymerization nature monomer which has two or more polymerization nature partial saturation radicals in intramoleculars, such as an esterification object with

polyhydric alcohol, such as dipentaerythritol; a polymerization nature partial saturation radical The polyfunctional (meta) acrylic-acid amide system polymerization nature monomer which it has two or more pieces; Diallyl phthalate, a polyfunctional allyl compound system polymerization nature monomer; (meta) acrylic-acid allyl compound, a divinylbenzene, etc. which have two or more polymerization nature partial saturation radicals in intramoleculars, such as diallyl maleate and diallyl fumarate, -- it can mention -- these -- one sort -- or two or more sorts are used.

[0016] As for the weight average molecular weight of the copolymer of this invention, 3,000 or more are desirable, and it is 100,000 or more still more preferably 10,000 or more more preferably. However, when a cross-linking monomer is used, molecular weight becomes very high and the determination of molecular weight by GPC cannot be performed. About the polymerization method of a monomer component, there is especially no limitation, for example, it can mention an oil-in-water type emulsion polymerization (it may be hereafter called an emulsion polymerization), a water-in-oil type emulsion polymerization (opposition suspension polymerization), a suspension polymerization, solution polymerization, aqueous polymerization, a bulk polymerization, etc. An emulsion polymerization is desirable among these polymerization methods. It is because handling viscosity is also low when the polymerization of the copolymer of the amount of macromolecules can be carried out in high concentration, and a production cost is also cheap.

[0017] A polymerization initiator is usually used for the polymerization of a monomer component. Heat decomposes this polymerization initiator, it is the matter made to generate a radical molecule, and an especially water-soluble initiator is used in an emulsion polymerization. as a polymerization initiator -- persulfate [, such as potassium persulfate, ammonium persulfate, and sodium persulfate,]; -- 2 and 2 - azobis (2-amidinopropane) dihydrochloride, and '4, 4' -- redox system polymerization initiators, such as a pyrolysis system initiator; hydrogen peroxide, an ascorbic acid and t-butyl hydroperoxide, a Rongalite and potassium persulfate and metal salts, such as - azobis (4-cyano pentanoic acid), ammonium persulfate, and a sodium hydrogensulfite, etc. -- it can mention -- these -- one sort -- or two or more sorts are used. [, such as a water-soluble azo compound; hydrogen peroxide]

[0018] As for an emulsion polymerization method, generally, it is desirable to carry out using an emulsifier. As an emulsifier, although there is nothing, especially limitation can mention an anion system surface active agent, the Nonion system surface active agent, a cation system surface active agent, an amphoteric surface active agent, high molecular surface active agents, these reactive surface active agents, etc., and may use them combining these, and the polymerization of it can also be carried out, for example, without using an emulsifier entirely depending on the case. As an anion system surface active agent, for example Sodium dodecyl sulfate, Potassium dodecyl sulfate, alkyl sulfate salt [, such as ammonium alkyl sulfate,]; -- sodium dodecyl polyglycol ethersulfate; -- sodium sulfo RISHINOETO; -- alkyl sulfonate [, such as a sulfonation paraffin salt,]; -- sodium dodecylbenzene sulfonate -- alkyl sulfonate [, such as alkali-metal sulfate of alkali phenol hydroxy ethylene,]; -- quantity alkylnaphthalenesulfonate; -- naphthalene sulfonic-acid formalin condensate; -- sodium laurate -- Triethanolamine oleate, Fatty-acid salt [, such as triethanolamine loon ETETO,]; Polyoxy alkyl ether sulfate salt; polyoxyethylene carboxylate sulfate salt; -- polyoxyethylene phenyl ether sulfate salt; -- succinic-acid dialkyl ester sulfonate; -- double association of a polyoxyethylene alkyl aryl sulfate salt etc. the reactant anion emulsifier which it had -- it can mention -- these -- one sort -- or two or more sorts are used.

[0019] as the Nonion system surface active agent -- a condensation product with aliphatic series monoglyceride; polyoxyethylene oxypropylene copolymer; ethyleneoxide and fatty amines, such as mono-laurate of polyoxyethylene-alkyl-ether; polyoxyethylene-alkyl-aryl-ether; sorbitan aliphatic series ester; polyoxyethylene sorbitan aliphatic series ester; glycerol, an amide, or an acid etc. -- it can mention -- these -- one sort -- or two or more sorts are used. as a giant-molecule surface active agent -- polyvinyl alcohol, its denaturation object; (meta) acrylic-acid system water soluble polymer; hydroxyethyl (meta) acrylic-acid system water soluble polymer; hydroxypropyl (meta) acrylic-acid system water soluble polymer; polyvinyl pyrrolidone, etc. -- it can mention -- these -- one sort -- or two or more sorts are used.

[0020] Although there is especially no limitation about the polymerization temperature in an emulsion polymerization, 0-100 degrees C is 40-95 degrees C still more preferably. Although there is especially no limitation also about polymerization time amount, it is 3 - 15 hours preferably. In case an emulsion polymerization is carried out, a hydrophilic solvent, an additive, etc. can be added in the range which does not have a bad influence on the physical properties of the copolymer obtained. As an approach of adding a monomer component to the emulsion polymerization system of reaction, there is especially no limitation and it can use a package addition method, a monomer component dropping test, the pre emulsion method, the power feed method, the seeding method, a multistage addition method, etc.

[0021] As for the nonvolatile matter in the emulsion obtained after an emulsion polymerization reaction, i.e., the copolymer of this invention, it is desirable that it is 60 or less % of the weight. It is because the viscosity of an emulsion is too high, so there is a possibility that distributed stability cannot be maintained but condensation may occur when a nonvolatile matter exceeds 60 % of the weight. Although there is especially no limitation about the mean particle diameter of the above-mentioned emulsion, it is 10nm - 1 micrometer preferably, and is 20-500nm still more preferably. Viscosity of an emulsion cannot become it high that the mean particle diameter of an emulsion is less than 10nm too much, distributed stability cannot be maintained, but there is a possibility of condensing. On the other hand, when it exceeds 1 micrometer, it is no longer an emulsion.

[0022] At the time of an emulsion polymerization, per [0.001] monomer component 100 weight section - **** for 2 weight sections are also good in a chain transfer agent because of molecular weight reduction. As a chain transfer agent, for example Halogenation alkane; n-dodecyl mercaptans, such as a carbon tetrachloride, bromoform, and BUROMO trichloroethane, tert-dodecyl mercaptan, an octyl mercaptan, tetradecyl mercaptan, Alkyl mercaptan, such as a hexadecyl mercaptan; N-butyl thioglycolate, Thioester, such as mono-thioglycolic acid alkyls, such as isooctyl thioglycolate and thioglycolic acid dodecyl; A methanol, Alcohols, such as ethanol and isopropanol; although an alpha-methyl-styrene dimer, TAPI Norian, a terpinene, a dipentene, etc. can be mentioned, it is not limited to these.

[0023] The copolymer of this invention has an acidic group in intramolecular, and is meltable in an alkali solution. And after dissolving in an alkali solution, when the hydrophobic radicals which consist of R originating in the alkenyl ether monomer shown by the general formula (1) meet strongly, the thickening nature of a solution increases. The copolymer of this invention can be blended and used for thickeners, such as for example, construction and a coating for building materials, a binder, printing ink, a paper application agent, and bentonite slurry, a synthetic water retention agent, the separation reduction agent for concrete, etc. using such a property.

[0024]

[Example] Although an example explains this invention to a detail further below, this invention is not limited to this. That it is especially only in below with the "section" and "%" shall express the "weight section" and "% of the weight", respectively, as long as there is no notice.

They are 182.8 ***** at the 4 Thu openings flask equipped with the <example A-1> agitator, the thermometer, and the condensator about the 50 mol addition product of ethyleneoxy radicals of the polyoxyethylene (3-methyl-3-butenyl) ether. The octadecyl isocyanate 47.26 section was dropped at homogeneity over 1 hour, agitating with the internal temperature of 60 degrees C. Churning was continued at 70 more degrees C for 4 hours, disappearance of the peak which originates in a hydroxyl group by the IR spectrum was checked, and it considered as the reaction terminal point. Next, the ion exchange water of the 750 sections was fed into the 3 Thu openings flask equipped with the agitator, the thermometer, and the condensator, and the above-mentioned reactant was supplied. Moisture was removed after 1-hour churning at 80 degrees C. It was made to dissolve in the tetrahydrofuran of the 300 sections, and centrifugal separation of the obtained slurry was carried out by 12000 rotations for 1 hour, and it was filtered through the filter paper. Except for the tetrahydrofuran, the urethane bond object of the octadecyl polyoxyethylene (3-methyl-3-butenyl) ether which is the purpose product was obtained from the filtrate as a wax-like solid-state by the evaporator.

[0025] The graph which shows IR measurement result to drawing 1 for the graph which shows the NMR measurement result of the compound obtained in the example A-1 is shown in drawing 2. The graph which shows IR measurement result to drawing 3 for the graph which shows the NMR measurement result of the 50 mol addition product of ethyleneoxy radicals of the polyoxyethylene (3-methyl-3-butenyl) ether used as a raw material for reference is shown in drawing 4. When drawing 1 and drawing 3 were compared, in drawing 1, the proton originating in the octadecyl radical which was not in drawing 3 appeared in the 0.8 to delta1.5 neighborhood. When drawing 2 and drawing 4 were compared, in drawing 2, the absorption (1600-1750cm⁻¹ neighborhood and 3350cm⁻¹ neighborhood) which the absorption (3100-3700cm⁻¹ neighborhood) originating in the hydroxyl group of the end of the 50 mol addition product of ethyleneoxy radicals of the polyoxyethylene (3-methyl-3-butenyl) ether which suited drawing 4 disappears mostly, instead originates in a urethane bond appeared.

[0026] Moreover, the graph which shows the GPC measurement result of the compound obtained in the example A-1 is shown in drawing 5. Drawing 5 shows that the molecular weight of the compound obtained in the example A-1 has distribution.

The 50 mol addition product 200 of ethyleneoxy radicals section of the <example A-2> polyoxyethylene (3-methyl-3-butenyl) ether and the dodecyl isocyanate 37 section were made to react by the same technique as an example A-1, and the urethane bond object of the dodecyl polyoxyethylene (3-methyl-3-butenyl) ether was obtained.

[0027] The 50 mol addition product 100 of ethyleneoxy radicals section of the <example A-3> polyoxyethylene (3-methyl-3-butenyl) ether and the hexyl isocyanate 11.1 section were made to react by the same technique as an example A-1, and the urethane bond object of the hexyl polyoxyethylene (3-methyl-3-butenyl) ether was obtained.

The 50 mol addition product of ethyleneoxy radicals of the polyoxyethylene (3-methyl-3-butenyl) ether was prepared for the 250 sections, and the 35.8 sections and the cyclohexane 100 section were prepared to the 4 Thu openings flask equipped with the <example A-4> agitator, the thermometer, and the condensator for methyl stearate. Agitating with the internal temperature of 100 degrees C, the cyclohexane was made to flow back and moisture was removed completely. Next, the tetrabutoxytitanium 2.96 section was supplied. Churning was continued at 100 more degrees C for 20 hours, disappearance of the peak which originates in methyl stearate by GPC measurement was checked, and it considered as the reaction terminal point. Next, the 3 sections of ion exchange water were thrown in, and it agitated at 100 degrees C for 1 hour. Except for moisture and a cyclohexane, the ester connective of the octadecyl polyoxyethylene (3-methyl-3-butenyl) ether which is the purpose product was obtained from the obtained slurry as a wax-like solid-state by the evaporator.

[0028] The graph which shows IR measurement result to drawing 6 for the graph which shows the NMR measurement result of the compound obtained in the example A-4 is shown in drawing 7. When drawing 6 and drawing 3 were compared, in drawing 6, the proton originating in the octadecyl radical which was not in drawing 3 appeared in the 0.8 to delta1.5 neighborhood. When drawing 7 and drawing 4 were compared, in drawing 7, the absorption (1650-1750cm⁻¹ neighborhood) which the absorption (3100-3700cm⁻¹ neighborhood) originating in the hydroxyl group of the end of the 50 mol addition product of ethyleneoxy radicals of the polyoxyethylene (3-methyl-3-butenyl) ether which suited drawing 4 disappears mostly, instead originates in an ester bond appeared.

[0029] Moreover, the graph which shows the GPC measurement result of the compound obtained in the example A-4 is shown in drawing 8. Drawing 8 shows that the molecular weight of the compound obtained in the example A-4 has distribution.

The ion-exchange-water 336 section, the sulfonic-acid ammonium salt 1.5 section of polyoxyethylene dodecylether, and the sodium chloride 0.038 section were supplied to the 4 Thu openings separable flask equipped with a <example B-1> agitator, a thermometer, a condensator, nitrogen installation tubing, and a dropping funnel. The nitrogen purge of the inside of a sink and a reaction container was gently carried out for nitrogen completely, agitating with the internal temperature of 68 degrees C. Next, the sulfonic-acid ammonium salt 1.5 section of polyoxyethylene dodecylether was dissolved in the ion-exchange-water 269 section, the mixture of the methacrylic-acid 40 section, the ethyl-acrylate 52.6 section, and the

urethane bond object 7.4 section of the octadecyl polyoxyethylene (3-methyl-3-butenyl) ether obtained in the example A-1 was thrown into this, it agitated and the pre emulsion was produced. Moreover, the ammonium persulfate 0.23 section was mixed in the ion-exchange-water 67.4 section, and the polymerization initiator water solution was produced. 5% of the above-mentioned pre emulsion was supplied to the reaction container, and the sodium-hydrogensulfite 0.017 section was supplied after 5-minute churning. Subsequently, it agitated for 20 minutes after feeding 5% of the above-mentioned polymerization initiator solution into a reaction container, and the initial polymerization was performed. The internal temperature of a reaction container was kept at 72 degrees C, and a remaining pre emulsion and a remaining polymerization initiator water solution were dropped at homogeneity over 2 hours. It supplied to the reaction container after washing driptank in the ion-exchange-water 26.5 section after dropping termination. After keeping the internal temperature at 72 degrees C and continuing churning for further 1 hour, it cooled, the reaction was completed and the emulsion polymer (1) of 30% of nonvolatile matters was obtained.

[0030] 1% alkali neutralization solution of an emulsion polymer (1) was prepared, and the pH and viscosity were measured. The result is shown in Table 1. 1% alkali neutralization solution put the emulsion of the two sections into the predetermined container by solid content conversion, diluted this with ion exchange water, subsequently, stirring with a stirring rod, added the sodium-hydroxide water solution of 0.5 conventions of the specified quantity, and prepared it as a total of 200 sections. Viscosity measured the viscosity of 25 degrees C by Rota No.4 and 30 rotations by the Brookfield viscometer. In addition, in Table 1, pH of 1% alkali neutralization solution of alkali fusibility meeting mold thickener ply mull TT-615 (loam - and made in - Haas) and viscosity were also written together.

[0031] In the <example B-2> example B-1, except having used the monomer component which consists of the methacrylic-acid 40 section, the ethyl-acrylate 52.9 section, and the urethane bond object 7.1 section of the dodecyl polyoxyethylene (3-methyl-3-butenyl) ether obtained in the example A-2 as a monomer component, the polymerization was performed like the example B-1, and the emulsion polymer (2) was obtained. Like the example B-1, 1% alkali neutralization solution of an emulsion polymer (2) was prepared, and the pH and viscosity (25 degrees C, Brookfield viscometer) were measured. The result is shown in Table 1.

[0032] In the <example B-3> example B-1, except having used the monomer component which consists of the methacrylic-acid 40 section, the ethyl-acrylate 52.3 section, and the ester connective 7.7 section of the octadecyl polyoxyethylene (3-methyl-3-butenyl) ether obtained in the example A-4 as a monomer component, the polymerization was performed like the example B-1, and the emulsion polymer (3) was obtained. Like the example B-1, 1% alkali neutralization solution of an emulsion polymer (3) was prepared, and the pH and viscosity (25 degrees C, Brookfield viscometer) were measured. The result is shown in Table 1.

[0033] In the <example B-1 of comparison> example B-1, except having used the monomer component which consists of the methacrylic-acid 40 section, the ethyl-acrylate 50 section, and the polyoxyethylene (3-methyl-3-butenyl) ether 6.5 section as a monomer component, the polymerization was performed like the example B-1, and the emulsion polymer (4) was obtained. Like the example B-1, 1% alkali neutralization solution of an emulsion polymer (4) was prepared, and the pH and viscosity (25 degrees C, Brookfield viscometer) were measured. The result is shown in Table 1.

[0034] In the <example B-2 of comparison> example B-1, except having used the monomer component which consists of the methacrylic-acid 35 section and the ethyl-acrylate 65 section as a monomer component, the polymerization was performed like the example B-1, and the emulsion polymer (5) was obtained. Like the example B-1, 1% alkali neutralization solution of an emulsion polymer (5) was prepared, and the pH and viscosity (25 degrees C, Brookfield viscometer) were measured. The result is shown in Table 1.

[0035]

[Table 1]

重合体	1%アルカリ中和水溶液	
	pH	粘度 (mPa·s)
実施例B-1	8.82	>20000
実施例B-2	8.15	17200
実施例B-3	7.56	16600
比較例B-1	7.76	1030
比較例B-2	7.69	460
プライマルII-615	6.82	4000

[0036]

[Effect of the Invention] It is new, and the copolymer concerning this invention is meltable in an alkali solution, and when it dissolves, it can raise the viscosity by leaps and bounds.

[Translation done.]